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Controlled oxidative synthesis of Bi nanoparticles and emission centers in bismuth glass nanocomposites for photonic application

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ABSTRACT

Here we demonstrate an oxidative process to control metallic bismuth (Bi^0) nanoparticles (NPs) creation in bismuth glass nanocomposites by using $K_2S_2O_8$ as oxidant and enhanced transparency of bismuth glasses. Formation of Bi^0 NPs has been monitored by their distinct surface plasmon resonance (SPR) band at 460 nm in the UV–visible absorption spectra. It is further confirmed by the transmission electron microscopy (TEM) images which disclose the formation of spherical Bi^0 NPs whereas the selected area electron diffraction (SAED) pattern reveals their crystalline rhombohedral phase. These glasses are found to exhibit visible and near infrared (NIR) luminescence bands at 630 and 843 nm respectively on excitation at 460 nm of the SPR band. It is realized that the luminescence center of bismuth species is an uncertain issue, however, it is reasonable to consider that the emission band at 630 nm is due to the combination of $^2D_{5/2} \rightarrow {}^4S_{3/2}$ of Bi^0 and $^2P_{3/2}$ (1) $\rightarrow {}^2P_{1/2}$ of Bi^{2+} transitions, and that of NIR emission band at 843 nm is attributed to the $^2D_{3/2} \rightarrow {}^4S_{3/2}$ of Bi^0 transition.

1. Introduction

In recent years, there has been an increasing interest in the synthesis of metallic nanoparticles and its surface plasmon resonance (SPR) band in the visible spectrum [1–3]. SPR band arises from the surface plasmon oscillation modes of conduction band electrons in metal nanoparticles (NPs), and strongly influences their linear and nonlinear optical response. SPR has the unique capacity to confine light in very small dimensions which could enable many new applications [1,2]. A lot of thrusts have been given on the study of surface plasmons, local field properties of metal NPs and their potential applications in plasmonics [1]. When various applications in plasmonics are concerned, development of well controlled synthetic methodologies is the most important factors and great challenges particularly in glass matrices [2]. Exploitation of glasses as encapsulating hosts for plasmonic metal nanoparticles (fabrication of matallo-dielectric nanocomposites) provides a prospect to create a variety of nanoscale devices with attractive properties caused by amalgamation of the properties of the glass host and the nanometal. Glass present some superior inherent advantage over other dielectrics, such as high transparency, higher homogeneity than that of other sintered materials, mechanical strength, ease of fabrication in desirable size and shape, ability to withstand high intensity radiation, and avoiding air oxidation of metal nanocomposites. Which make glasses excellent encapsulating hosts for metal NPs for practical applications [4–7].

There is a renewed interest in the bismuth glasses due to many reasons, some of them are indicated below. Bismuth glass is one of the most important amongst the heavy metal oxide (HMO) glasses due to their several inherent properties such as high refractive index, wide transmission window, and broad band near infrared (NIR) luminescence. [8–11]. In recent time, bismuth glasses have attracted attention of various researchers as a very important optical material from the view point of its photoluminescence properties for photonics and optoelectronic applications. In bismuth glass, the various oxidation states of bismuth such as Bi^{5+}, Bi^{3+}, Bi^{2+}, Bi^{+} and Bi^0 are coexist [8]. Therefore, the emission centers due to various bismuth ions are controversial issue and need further investigation.

However, bismuth oxide glasses are usually obtained in dark-brown or black color, which deepens with increasing Bi_2O_3 content and when melted above 1000 °C [9,10]. This limits to a great extent the application of bismuth oxide glasses for optical and photonic purposes. Therefore, controlled synthesis of bismuth (Bi^0) nanoparticles (NPs) in bismuth glasses and colorless bismuth glasses are very important both academically as well as technological point of views. In our previous work [12], we have demonstrated the controlled synthesis of Bi^0 NPs in bismuth glass using $KClO_4$ and KNO_3 oxidants. To the best of our knowledge, there is no previous report on the control synthesis of Bi^0 NPs in bismuth glasses by applying the oxidation technique using $K_2S_2O_8$.

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In view of above and extension of our previous work [12], in this paper we report the synthesis of Bi^0 NPs in the B_2O_3–ZnO–Bi_2O_3–SiO_2–K_2O glass system by controlling the auto-thermo reduction of Bi_2O_3 using $K_2S_2O_8$ as oxidizing agent and evaluation of their properties by UV–Vis spectroscopy, transmission electron microscopy (TEM), selected area electron diffraction (SAED) analysis and luminescence measurement.

2. Experimental section

Glass samples were synthesized by conventional melting and quenching techniques as described in our previous work [12], using bismuth trioxide, Bi_2O_3 (Loba Chemie), boric acid, H_3BO_3 (Loba Chemie), zinc oxide, ZnO (Loba Chemie), potassium carbonate, K_2CO_3 (Loba Chemie), silicon dioxide, SiO_2 (Bremthaler/Quarzitwerk) and potassium peroxodisulphate, $K_2S_2O_8$ (Merck) as raw materials. The raw materials for 25 g glass of composition (mol%): $32.32B_2O_3$–$33.47ZnO$–$11.44Bi_2O_3$–$17.74SiO_2$–$(5.03-x)K_2O$–$xK_2S_2O_8$, where x is the equivalent amount of K_2O obtained from the source of $K_2S_2O_8$ (where x is 0, 0.0011, 0.0026, 0.0053, 0.0110 and 0.0158). All the melting and annealing conditions were same as previous work [12]. Samples of 2 ± 0.01 mm thickness were prepared by cutting, grinding and polishing for optical measurements.

The UV–Vis absorption spectra in the range of 350–700 nm were recorded using a double beam UV–visible spectrophotometer (Lambda 20, Perkin–Elmer) at an error of ±0.1 nm. The fluorescence spectra were measured for all the samples at an error of ±0.2 nm with a Perkin Elmer Luminescence Spectrophotometer (Model LS55) exciting at 460 nm using a Xenon lamp as the excitation source and a photomultiplier tube (PMT) as detector. The TEM and SAED images were taken using a FEI instrument (Tehnai-30, ST G^2) operating at an accelerating voltage of 300 kV.

3. Results and discussion

The major problem for preparation of bismuth containing transparent glasses is the graying or blackening when melted above 1000 °C. The intensity of greying or blackening increases with increase in melting temperature as well as Bi_2O_3 content. It is due to auto-thermo reduction of Bi^{3+} ions to bismuth metal (Bi^0) during the course of melting process. The reduction of Bi_2O_3 occurs through the following thermal decomposition reaction [9,10]

$$2Bi_2O_3 \leftrightarrow 4Bi^0 + 3O_2 \uparrow \quad (1)$$

In the above equilibrium reaction, the metallic Bi^0 is formed with the release of oxygen. When the strong oxidizing agent, such as $K_2S_2O_8$, is added as a source of K_2O in the glass composition, it increases the oxygen partial pressure as a result of its thermal decomposition during melting process which is as follow [13]

$$K_2S_2O_8 \rightarrow K_2O + 2SO_3 \uparrow + 1/2O_2 \uparrow \quad (2)$$

$$2SO_3 \rightarrow 2SO_2 \uparrow + O_2 \uparrow \quad (3)$$

Therefore, the reaction of the Eq. (1) proceeds in the reverse direction due to reactions of the Eqs. (2) and (3). In our previous work [12], we have used $KClO_4$ and KNO_3 as oxidants to suppress the formation of Bi^0 NPs in these glasses. Similarly, by comparing the standard reduction potentials [14] as listed in Table 1, it is clear that the standard potential of $S_2O_8^{2-}/SO_4^{2-}$ is much higher (2.01 V) than that of Bi^+/Bi^0 (0.50 V), Bi^{3+}/Bi^0 (0.31 V), Bi^{3+}/Bi^+ (0.20 V) and Bi^{3+}/Bi^{2+} (<0.20 V) species, so it easily favors the backward reactions of the Eq. (1) and suppressed the auto-thermo decomposition of Bi_2O_3. It results the controlled formation of Bi^0 NPs and the glasses gradually become more transparent with increasing $K_2S_2O_8$ concentration. This fact could be visualized clearly by the remarkable changes in the transparency of the resultant glasses as shown in Fig. 1. As the reduction potentials of various valence states of bismuth are very close to each other, therefore, it is very difficult to predict which valence state of bismuth ion will form during melting process.

Table 1
Redox reaction and reduction potential of peroxodisulphate and bismuth ions.

Redox reaction	Reduction potential (E^o, V)
$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	2.01
$Bi^+ + e^- = Bi^0$	0.50
$Bi^{3+} + 3e^- = Bi^0$	0.31
$Bi^{3+} + 2e^- = Bi^+$	0.20
$Bi^{3+} + e^- = Bi^{2+}$	<0.20[a]

[a] Exact value is not available.

The UV–Vis absorption spectra of bismuth glasses are shown in Fig. 2. The observed broad absorption spectra show maxima at 460 nm. Wang et al. [15] have synthesized poly (vinylpyrroldone) (PVP) stabilized bismuth nanoparticles (NPs) and found absorption peak at 281 nm associated with Bi^0 NPs. Gutiérrez and Henglein [16] have prepared nanometer-sized particles of bismuth by the radiolytic reduction of aqueous solutions of bismuth perchlorate. They observed absorption spectrum of colloidal bismuth at 253 nm. Corain et al. [1] have reported the absorbance band of Bi^0 NPs in the host water (RI = 1.33) around 400 nm. Recently, some studies have carried out for the absorption band of metallic bismuth in various glass matrices [17–19]. Peng et al. [17] have found a broad absorption peak at around 465 nm for Bi_2O_3 contained glasses and assigned the peak as surface plasmon resonance (SPR) of metallic bismuth. Romanov et al. [18] have observed two broad absorption peaks at 475 and 443 nm for two different glasses of bismuth borate and bismuth potassium phosphate glasses respectively. They designated the peaks as the absorption due to metallic bismuth. Bishay [19] observed similar broad absorption at 515 nm due to elementary Bi in bismuth borate glass after γ-irradiation.

In this study, the glass has higher RI (1.76) and shows an absorption band at 460 nm. From above discussion, it is clear that the absorption at 460 nm is due to SPR of metallic bismuth nanoparticles [1,17–19]. Khonthon et al. [11] and Singh et al. [12] have also reported such absorption band of Bi^0 NPs at 460 nm in the different glass matrices, which is analogous to this result.

The SPR is a characteristic of metal nanoparticles embedded in a dielectric host and is attributed to the collective oscillation of electrons in response to optical excitation. The SPR of a spherical particle gives an absorbance band centered at a wavelength, λ, which can be expressed by the relation [20]

$$\lambda^2 = 4\pi^2 c^2 m_o \varepsilon_o (\varepsilon_m + 2n_o^2)/Ne^2 \quad (4)$$

where c is the velocity of light, m_o is the charge carrier particle mass, N is the charge carrier particle concentration, e is the charge of the electron, ε_m is the optical dielectric function of the metal, n_o is the refractive index (RI) of the host material and ε_o is the free-space permeability.

ω_d is the damping frequency, which is related to the mean free path of the conduction electrons (R_{bulk}) and v_f is the velocity of electrons at the Fermi energy. The most important parameter affecting ω_d is the particle size and it can be represented by the following equation [17]:

$$\omega_d = v_f/R_{bulk} \quad (5)$$

It can be seen from Eq. (5) that a decrease in particle size leads to an increase in ω_d, which is causing the band to broaden and the maximum intensity to decrease.